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Molecular Transport in Ionic Polymer Membranes Under an Applied Voltage

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14. ABSTRACT
Herein, we present direct measurements of ion dynamics of 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (EMIm-TFSI) in an operating EDLC with electrodes composed of porous nanosized carbide-derived carbons (CDCs) and non-porous onion-like carbons (OLCs) with the use of in situ infrared spectroelectrochemistry. For CDC electrodes, IL ions (both cations and anions) were directly observed entering and exiting CDC nanopores during charging and discharging of the EDLC. Conversely, for OLC electrodes, IL ions were observed in close proximity to the OLC surface without any change in the bulk electrolyte concentration

15. SUBJECT TERMS
polymer, capacitor, ATR spectroscopy, in situ, ionic liquid

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Yossef Elabd
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Report Title

Molecular Transport in Ionic Polymer Membranes Under an Applied Voltage

ABSTRACT

Herein, we present direct measurements of ion dynamics of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI) in an operating EDLC with electrodes composed of porous nanosized carbide-derived carbons (CDCs) and non-porous onion-like carbons (OLCs) with the use of in situ infrared spectroelectrochemistry. For CDC electrodes, IL ions (both cations and anions) were directly observed entering and exiting CDC nanopores during charging and discharging of the EDLC. Conversely, for OLC electrodes, IL ions were observed in close proximity to the OLC surface without any change in the bulk electrolyte concentration during charging and discharging of the EDLC. This provides experimental evidence that charge is stored on the surface of OLCs in OLC EDLCs without long-range ion transport through the bulk electrode. In addition, for CDC EDLCs with mixed electrolytes of IL and propylene carbonate (PC), the IL ions were observed entering and exiting CDC nanopores, while PC entrance into the nanopores was IL concentration dependent. This work provides direct experimental confirmation of EDLC charging mechanisms that previously were restricted to computational simulations and theories. The experimental measurements presented here also provide deep insights about the molecular level transport of IL ions in EDLC electrodes that will impact the design of materials for electrical energy storage.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 4.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper	
11/22/2013	1.00	Francis W. Richey, Boris Dyatkin, Yury Gogotsi, Yossef A. Elabd. Ion Dynamics in Porous Carbon Electrodes in Supercapacitors Using in Situ Infrared Spectroelectrochemistry, Journal of the American Chemical Society (08 2013)
11/22/2013	3.00	Francis W. Richey, Yossef A. Elabd. In Situ Molecular Level Measurements of Ion Dynamics in an Electrochemical Capacitor, The Journal of Physical Chemistry Letters (11 2012)
11/22/2013	2.00	F. W. Richey, Y. A. Elabd. In Situ Spectroscopic Measurements of Individual Cation and Anion Dynamics in a RuO2 Electrochemical Capacitor, Journal of the Electrochemical Society (04 2013)
TOTAL:	**3**	

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Received 1st Place Award in 2011 ECS Annual Meeting poster competition

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Francis W. Richey	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Yossef A. Elabd	0.08	
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

1. In Situ Molecular Level Measurements of Ion Dynamics in an Electrochemical Capacitor

Improving the energy storage capability of batteries and capacitors is inherently dependent on clarifying our understanding of ion dynamics of advanced electrolytes in a variety of materials. Herein, we report a new attenuated total reflectance - surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) technique that can selectively and simultaneously measure both cation and anion transport of an ionic liquid (1-ethyl-3-methylimidazolium triflate (EMIm-Tf)) in a functioning electrochemical pseudocapacitor (actuator). This new capacitor-spectroscopy technique was utilized to probe the gold current collector/RuO_2 electrode interface during both square wave and cyclic voltammetry experiments. Results show that the cations and anions transport as aggregates and the cation dominates and dictates the direction of ion transport in these devices. Results also show ion dynamics in pseudocapacitors are a diffusion-limited process.

2. In Situ Spectroscopic Measurements of Individual Cation and Anion Dynamics in a RuO_2 Electrochemical Capacitor

Improving the energy storage capability of electrochemical capacitors is inherently dependent on clarifying our understanding of ion dynamics of advanced electrolytes in a variety of materials. Herein, we apply a new in situ infrared spectroscopy technique to selectively and simultaneously measure both cation and anion dynamics of an ionic liquid (1-ethyl-3-methylimidazolium triflate (EMIm-Tf)) in a functioning RuO_2 capacitor. The individual cation and anion dynamics of EMIm-Tf are measured as a function of step voltage input, voltage scan rate, and RuO_2 content in the electrode. Results show that cations and anions transport as aggregates and cations are the dominant charge carrying species. Also, the ratio of cations to anions in the cathode during charge storage increases with increasing step voltage input and RuO_2 content in the electrode. In addition to changes in the cation to anion distribution, the concentration of both cations and anions increases and the rate of change of cations and anions increases as the porosity of the RuO_2 electrode increases, which all correspond to an increase in the volumetric capacitance. Cyclic voltammetry, in conjunction with infrared spectroscopy experimental results, confirm that charge storage, as well as cation and anion transport both follow a diffusion-limited behavior.

3. Ion Dynamics in Porous Carbon Electrodes in Supercapacitors Using in situ Infrared Spectroelectrochemistry

Electrochemical double layer capacitors (EDLC), or supercapacitors, rely on electrosorption of ions by porous carbon electrodes and offer a higher power and a longer cyclic lifetime compared to batteries. Ionic liquid (IL) electrolytes can broaden the operating voltage window and increase the energy density of EDLCs. Herein, we present direct measurements of ion dynamics of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI) in an operating EDLC with electrodes composed of porous nanosized carbide-derived carbons (CDCs) and non-porous onion-like carbons (OLCs) with the use of in situ infrared spectroelectrochemistry. For CDC electrodes, IL ions (both cations and anions) were directly observed entering and exiting CDC nanopores during charging and discharging of the EDLC. Conversely, for OLC electrodes, IL ions were observed in close proximity to the OLC surface without any change in the bulk electrolyte concentration during charging and discharging of the EDLC. This provides experimental evidence that charge is stored on the surface of OLCs in OLC EDLCs without long-range ion transport through the bulk electrode. In addition, for CDC EDLCs with mixed electrolytes of IL and propylene carbonate (PC), the IL ions were observed entering and exiting CDC nanopores, while PC entrance into the nanopores was IL concentration dependent. This work provides direct experimental confirmation of EDLC charging mechanisms that previously were restricted to computational simulations and theories. The experimental measurements presented here also provide deep insights about the molecular level transport of IL ions in EDLC electrodes that will impact the design of electrode materials' structure for electrical energy storage.

Technology Transfer